

# PATENT SPECIFICATION

NO DRAWINGS

976,240



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Date of Application and filing Complete Specification Dec. 28, 1962.

No. 48903/62.

Application made in Germany (F35698 IVd;39b) on Dec. 30, 1961.

Complete Specification Published Nov. 25, 1964.

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Index at acceptance:—C3 R(32C6, 32C9, 32C10, 32C11, 32C12, 32D1, 32D4, 32D5, 32D6, 32E2, 32F); B2 E(1A, 1H)

International Classification:—C 08 g (C 08 j, D 06 m)

## COMPLETE SPECIFICATION

### A Process for the Production of Polymers Comprising Urethane and Semi-carbazide Groupings

SPECIFICATION NO. 976,240

The inventors of this invention in the sense of being the devisers thereof within the meaning of Section 16 of the Patents Act, 1949 are:— Wilhelm Thoma, Roggendorferstrasse 49, Köln-Flittard, Germany, Heinrich Rinke, Saarlauterner Strasse 15, Leverkusen, Germany, Harald Oertel, Lindenstrasse 12, Leverkusen, Germany; all of German Nationality.

THE PATENT OFFICE

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15 polymers which can be formed from a solution, which polymers can for example be used for highly elastic coatings on any desired supports (more especially on textiles) or for obtaining fibres. For this purpose, use is made of two basically different methods, namely the two-component process and the one-component process.

20 In the two-component process, mixtures or solutions of polyisocyanates with polyesters which comprise hydroxyl groups and which may be modified with isocyanates are applied to the support material and the coating is cured on the said material. It is also known with this process to introduce isocyanate-modified polyesters containing hydrazide groups.

25 One disadvantage of the two-component process is the fact that the storage capacity, the so-called pot life, of the mixtures of solutions which contain polyisocyanates as well as compounds with active hydrogen atoms is quite short. Another disadvantage is that the curing, which must be carried out quickly for series production, is carried out at high temperature on the support which is to be coated.

30 In the one-component process a prepared [Price 4s. 6d.]

with the free NCO-groups. This latter reaction takes place in the presence of catalysts capable of causing the polymerisation of NCO-groups and for sufficient time for the solution to reach a required viscosity, the reaction then continuing after adding a monohydric alcohol and/or amine until no more NCO-groups are present.

Such coatings have a soft textile "handle" but show relatively low resistance to rubbing with a pigment filling.

Another process for the production of isocyanate polyaddition products by the one-component process consists in reacting, in solution, initial adducts comprising NCO-groups with polyhydrazides, for example N,N'-diaminourea. Pigmented coatings prepared therefrom show a small degree of abrasion, but are stiff in a textile sense on account of the high modulus of the elastometer. Furthermore, they do not permit the incorporation of high filter contents (i.e. 50 to 100% by weight).

Despite these defects, the prior known one-component processes have the invaluable advantage of having any desired pot life by comparison with the two-component process. Consequently, it is surprising that there could

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## COMPLETE SPECIFICATION

### A Process for the Production of Polymers Comprising Urethane and Semi-carbazide Groupings

We FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT of Leverkusen-Bayerwerk, Germany, a body corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of polymers comprising urethane and semi-carbazide groupings.

It is known that it is possible by the isocyanate poly-addition process to produce polymers which can be formed from a solution, which polymers can for example be used for highly elastic coatings on any desired supports (more especially on textiles) or for obtaining fibres. For this purpose, use is made of two basically different methods, namely the two-component process and the one-component process.

In the two-component process, mixtures or solutions of polyisocyanates with polyesters which comprise hydroxyl groups and which may be modified with isocyanates are applied to the support material and the coating is cured on the said material. It is also known with this process to introduce isocyanate-modified polyesters containing hydrazide groups.

One disadvantage of the two-component process is the fact that the storage capacity, the so-called pot life, of the mixtures of solutions which contain polyisocyanates as well as compounds with active hydrogen atoms is quite short. Another disadvantage is that the curing, which must be carried out quickly for series production, is carried out at high temperature on the support which is to be coated.

In the one-component process a prepared

polymer which does not contain any free NCO-groups or any free isocyanate reactant, is usually obtained in solution by the isocyanate polyaddition process and is applied to the support. Such solutions of isocyanate polyaddition products are for example obtained when polyhydroxy compounds are reacted with an excess (calculated on the free OH-groups present) of polyisocyanates and the reaction products comprising NCO-groups are reacted in a solvent (which is neutral with respect to NCO-groups) with a smaller quantity of polyhydric alcohols then is required for the complete reaction with the free NCO-groups. This latter reaction takes place in the presence of catalysts capable of causing the polymerisation of NCO-groups and for sufficient time for the solution to reach a required viscosity, the reaction then continuing after adding a monohydric alcohol and/or amine until no more NCO-groups are present.

Such coatings have a soft textile "handle" but show relatively low resistance to rubbing with a pigment filling.

Another process for the production of isocyanate polyaddition products by the one-component process consists in reacting, in solution, initial adducts comprising NCO-groups with polyhydrazides, for example N,N'-diaminourea. Pigmented coatings prepared therefrom show a small degree of abrasion, but are stiff in a textile sense on account of the high modulus of the elastometer. Furthermore, they do not permit the incorporation of high filter contents (i.e. 50 to 100% by weight).

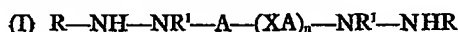
Despite these defects, the prior known one-component processes have the invaluable advantage of having any desired pot life by comparison with the two-component process. Consequently, it is surprising that there could

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be discovered a one-component process for the production of highly elastic shaped elements or coatings on any desired supports by the isocyanate polyaddition process which simultaneously permits the production of soft coatings which can be highly filled or loaded and which are very resistant to rubbing.

In our Specifications Nos. 917450 and 914609, we have described processes for the production of polymers by forming an isocyanate-modified polyhydroxyl compound and reacting this isocyanate-modified polyhydroxyl compound with a dihydrazide.

The present invention provides a process



in which A is a  $\text{—CO—}$ ,  $\text{—CS—}$  or  $\text{—SO}_2\text{—}$  group; R and R' are hydrogen atoms or alkyl or aryl radicals; X is an alkylene, arylene or aralkylene radical which may be interrupted by hetero atoms or X is an  $\text{—OYO—}$  or  $\text{—NH—Y—NH—}$  radical in (I) or a  $\text{—YO—}$  or  $\text{—Y—NH—}$  radical in (II) or (III); Y is a divalent organic radical; and  $n$  is 0 or 1.

The polymers prepared in accordance with the invention are usually in the form of solutions and are intended for coatings and impregnation purposes, for the preparation of films or coatings and which are capable of being stored. Coatings, films and coverings prepared therefrom are distinguished by a particularly high resistance to abrasion and with a simultaneously soft handle, even with a high pigment content.

The production of the compounds containing terminal NCO-groups is effected by reacting polyhydroxyl compounds with an excess of polyisocyanates (calculated on the OH-groups present) in a manner known *per se*. One preferred series of NCO-group containing compounds is obtained by reacting a polyhydroxy compound with such a quantity of polyisocyanate that 125 to 250 parts by weight of NCO-groups in the polyisocyanate are present to 34 parts by weight of hydroxy groups in the polyhydroxy compound.

The following are examples of polyhydroxyl compounds: polyesters, polyester amides, polyester urethanes, polyester ethers, polyethers, polythioethers, polyacetals, polyester acetals and polyether acetals with molecular weights between 500 and 5000. Specifically to be mentioned are polyesters from ethylene glycol, propylene glycol, butanediol, hexanediol, dimethyl propane-1,3-diol, methyl hexanediol, bis-hydroxymethyl cyclohexane, phenylene-1,4-bis-hydroxyethyl ether, trimethylol propane and adipic acid, methyladipic acid, suberic acid, sebacic acid, tere-

phthalic or isophthalic acids, hexahydroterephthalic acid, maleic acid, polyester amides from diol diamides and the aforementioned dicarboxylic acids for example adipic acid diethanolamide, terephthalic acid-bis-N-methylpropanolamide; polyester urethanes from polyesters containing short-chain OH-groups (molecular weight 200 to 2000) and a diisocyanate, such as diphenyl methane-4,4'-diisocyanate, toluylene-2,6- or 2,4-diisocyanates, alkylated toluylene diisocyanates and hexane-1,6-diisocyanate; polyester ethers from diethylene or triethylene glycols, phenylene-1,4-bis-hydroxyethyl ethers, 2,2-diphenyl propane-4,4-bis-hydroxyethyl ether, 4,4-dihydroxy dibutyl ether, hexanediol polyethers or mixed ethers of hexanediol and methyl hexanediol with molecular weights from 200 to 2000 and the aforementioned dicarboxylic acids; polyethers of ethylene oxide, propylene oxide, tetrahydrofuran, hexanediol, methyl hexanediol and bis-hydroxymethyl cyclohexane and mixtures thereof; polythioethers of thiodiglycol, possibly with addition of other dihydric alcohols; polyacetals of hexanediol, methyl hexanediol, hydroxyethylated hexanediol and formaldehyde, polyester acetals from adipic acid, bis-hydroxyhexyl ester and formaldehyde or from mixed esters of hexane diol and methyl hexanediol/ adipic acid with formaldehyde, polyether acetals from polyethers and formaldehyde, for example hexanediol polyethers with a molecular weight of 200 to 2000 and formaldehyde. In addition to the aforementioned polyhydroxy compounds of relatively high molecular weight, it is possible concurrently to employ simple glycols.

Polyisocyanates suitable for the reaction with these polyhydroxy compounds are for example diphenyl methane-4,4'-diisocyanate, naphthylene-1,5-diisocyanate, 2,2'-diphenyl dimethyl methane-4,4'-diisocyanate, toluylene-2,4- and/or 2,6-diisocyanates, tolidine-

4,4'-diisocyanate, cyclohexane-1,4-diisocyanate, alkylated phenylene-1,3-diisocyanates, alkylated diphenyl methane diisocyanates and 4,4'-bis(isocyanatophenyl) thiophosphate.

5 Preferably 125—250 parts by weight of NCO-groups in the polyester are present for 34 parts by weight of hydroxyl groups in the polyhydroxy compound and the reaction is preferably carried out between 80 and 10 150°C., advantageously between 80 and 130°C., in the melt or with the use of solvents which are inert with respect to NCO-groups.

Butyl acetate, ethyl acetate, dipropyl ether, dioxane, tetrahydrofuran, chlorobenzene 15 and dichlorobenzene are mentioned as examples of solvents which are inert with respect to NCO-groups.

20 The isocyanate-modified polyhydroxy compounds containing terminal NCO-groups are reacted according to the invention in a first reaction step with only such a quantity of polyhydric alcohols in the melt or in solution that 10 to 90% of the NCO-groups present are left.

25 Butanediol, hexanediol diglycol, thiodiglycol, phenylene-1,4-bis-hydroxyethylether, short-chain polyesters with OH-groups and piperazine dicarboxylic acid bis-hydroxyethyl esters are examples of polyhydric 30 alcohols. Higher polyhydric alcohols such as trimethylol propane can be concurrently used.

35 The reaction with the polyhydric alcohol is usually carried out at temperatures between 50 and 150°C. and more especially between 70 and 110°C.

40 Examples of solvents for carrying out this first reaction stage in solution are those solvents which are neutral with respect to NCO-groups and which are used in the production of the isocyanate-modified polyhydroxy compounds, which solvents have sufficient 45 dissolving power for the said compounds and the polyaddition products (prepolymer) formed in the first stage. These solvents should not be used in too large a quantity as they are a poor dissolving agent for the final reaction products, i.e. the elastomers.

50 In a second reaction stage, the reaction products still comprising NCO-groups are reacted with hydrazide compounds of the above formulae, preferably after addition of those solvents which have good dissolving power for the end products and the hydrazide compounds, (for example dimethyl formamide, dimethyl acetamide or dimethyl sulfoxide). The reaction is usually carried out 55 at temperatures between 0 and 50°C., especially between 10 and 20°C., with 90 to 110%, (calculated on the NCO-content which is determined experimentally) and more especially with 100% of the calculated quantity. If 60 excess of hydrazide compound is used, it is possible to avoid an undesirable swelling of the reaction product. On the other hand, if 65 excess of the hydrazide is not used, it is

desirable for the free NCO groups still present to be reacted with a monoamine or monohydric alcohol or with a monohydrazide which contains no other active hydrogen-containing group in the molecule, for example with isobutylamine, ethyl alcohol or hydrazomonocarboxylic acid ethyl ester, which act as chain-breaking agents. Any excess of the chain-breaking agent can be 70 reacted in convenient manner by addition of pyrocarbonic acid diethyl ester to form inert products. 75

The following are mentioned as examples of the hydrazide compounds which can be used according to the invention, singly or in admixture: N,N'-diaminourea, oxalic acid hydroxy hydrazide; the dihydrazides of oxalic acid, malonic acid, succinic acid, adipic acid, isophthalic acid, piperazine-dicarboxylic acid and iminodicarboxylic acid; ethylene- and 85 butylene-bis-carbanilic acid esters, hexane-, butane- and xylylene-1,3-bis-semicarbazides, diguanyl ethylene,  $\omega$ -aminocaproic acid hydrazide,  $\omega$ -aminobutyric acid hydrazide,  $\omega$ -hydroxy caproic acid hydrazide,  $\omega$ -hydroxy 90 butyric acid hydrazide, tartaric acid dihydrazide and  $\omega$ -hydroxy butyric acid- $\beta$ -hydroxy ethyl hydrazide.

The viscous products which are obtained can easily yield solid content of 20 to 50% 95 by diluting or thickening the solution. The viscosity of the solutions is between 10 and 1000 poises at 20°C.

Coloured pigments or fillers, for example titanium dioxide, talcum or kaolin, age resistors and ultra-violet absorbers can be incorporated into the solutions before the shaping, as can also spirit-soluble or fat-soluble dye-stuffs. 100

The polymers which can be formed from the solution can be employed for coatings on any desired supports, more especially on textiles. The coating with a storable "one pot solution" free from NCO-groups can be effected in various ways, for example by application with a doctor blade, by means of rollers, by dipping, impregnating, pouring or spraying. In order to evaporate the solvent, the coated support is brought to high temperature, for example 60 to 150°C., 115 more especially 80 to 130°C. for a short time. The coated or impregnated dried web can then be reeled, if desired after passing between cooling cylinders. The products of the process are more especially suitable for the manufacture of waterproof clothing, all types of tarpaulins and as packing material. 120

By using, in the production of the polymers, those solvents which can be emulsified with water or by dissolving the polymer subsequently in such a solvent, the elastic material can also be used as an emulsion. It is possible after suitable dilution also to treat three-dimensional, irregular fibre fleeces of wool, cotton, staple rayon or other natural 130

End of page

or synthetic fibres with the elastomer solution or with the said emulsion, by dipping, saturating, spraying or impregnating and in this way to obtain unwoven textile sheet formations. Furthermore, it is possible with the elastomer solutions or emulsions prepared according to the invention to apply final coats to synthetic plastics, more especially to softened polyvinyl chloride foils, or to line for example metallic containers. In addition, stocking made for example from polyamides can be given a ladder-proof finish and nets or net yarns can be coated to give high-knot strength.

Elastomeric filaments can also be spun from the elastomer solutions by dry-spinning or wet-spinning processes. The spinning is effected from spinning nozzles into a spinning shaft through which hot air is flowing or by spinning the solution into a suitable precipitation bath.

The elastomer solutions obtained according to the invention can be stored and are distinguished from known polyurethane solutions used for coating purposes by the fact that they do not have to be used for further processing immediately after they have been produced, i.e. necessarily at their place of manufacture.

By comparison with other elastomer solutions, these can be highly pigmented, 50 to 100% by weight based on the plastic content of the solution, and yield coatings with a good handle, good resistance to weather, good stability with respect to alkalis and solvents (such as benzene and trichlorethylene or perchlorethylene) and have high tensile strength and resistance to further tearing. They are also distinguished from others by exceptional resistance to abrasion.

The following Examples illustrate the invention:

#### EXAMPLE 1

150 Grams of a polyester of ethylene glycol and adipic acid (OH-number 56) were dehydrated for one hour at 130°C. *in vacuo* and heated with 41.6 g. of diphenyl dimethyl methane-4,4'-diisocyanate for 60 minutes at

Thickness	- - - - -	0.08 mm.
Tensile Strength	- - - - -	385 kg/cm <sup>2</sup>
Elongation	- - - - -	700%
Modulus 20% elongation	- - - - -	14.0 kg/cm <sup>2</sup>
Modulus 300% elongation	- - - - -	50 kg/cm <sup>2</sup>
Resistance to further tearing according to Graves 24	- - - - -	24 kg/cm
Micro-hardness	- - - - -	52

#### EXAMPLE 2

65.0 Grams of a polyester obtained from diethylene glycol and adipic acid (OH-number 43.2) and 50 g. of a polyester obtained from ethylene glycol and adipic acid (OH-number 56) were dehydrated for 1 hour *in vacuo* at 130°C. and heated with 17.8 g. of toluylene diisocyanate (70/30 isomer mix-

110°C. After cooling the melt to 75°C., 0.70 g. of butane-1,4-diol was added and the melt was thereafter taken-up in 90 g. of dry chlorobenzene at a temperature of 80°C. The solution was kept for 15 minutes at 75 to 80°C. and then cooled to 20°C. The solution had an NCO-number of 2.24. After dilution with 180 g. of dimethyl formamide, an NCO-number of 1.05 was found.

A solution of 3.42 g. of carbodihydrazide in 200 g. of dimethyl formamide at 70°C. was prepared and introduced dropwise while stirring at 0 to 5°C. into 307 g. of the said solution. In order to avoid a swelling of the polymer, the addition reaction was stopped by adding 1.0 g. of hydrazomoncarboxylic acid ethyl ester in 15 g. of dimethyl formamide. The excess stopping agent was transformed by adding 1.5 ml. of pyrocarbonic acid diethyl ester in 5 g. of dimethyl formamide into hydrazodicarboxylic acid diethyl ester. The 24.7% solution was concentrated to 39% by distilling off solvents *in vacuo*. The viscosity was then 480 poises (20°C.).

500 Grams of this solution were ground with 160 g. of kaolin, 20 g. of titanium dioxide and 20 g. of an organic pigment dye-stuff on a one-cylinder colour mill and applied with a doctor blade to a web of cotton fabric. In order to evaporate the solvents, the coated web was conducted through a drying cabinet at a temperature of 80°C. In order to judge the storability of the solution, this was applied once again after being stored for 8 weeks at 30°C.; the same textile properties were observed. Using an eccentric disc provided with fine emery paper and running under a load of 200 g., the abrasion after 500 revolutions was 7.5 mg. (A coating prepared according to Example 1 of U.K. Specification No 908188, likewise by a one-component method, had an abrasion of 25 to 35 mg.) The breaking factor under bending was 100,000 at 20°C. and 50,000 to 65,000 at -20°C. Resistance to weather and tropical influences was good and the light fastness was very good. The unpigmented film had the following properties:

ture) for 50 minutes at 110°C. The melt was dissolved in 80 g. of chlorobenzene, 0.99 g. of phenylene-1,4-bis-hydroxyethyl ether was added and the solution was heated for 25 minutes at 80°C. After cooling, to 20°C., the solution was diluted with 330 g. of dimethyl formamide, NCO-content of the solution 0.62%.

A solution of 2.68 g. of hexane-bis-semi-carbazide and 3.65 g. of succinic acid dihydrazide in 20 g. of water was added dropwise to 500 g. of the aforementioned solution while mixing well and at 5 to 10°C. A viscous solution was formed, which had a viscosity of 260 poises at 20°C. after being concentrated to 35% solid content.

Pigments and fillers were added to the solution in the manner described in Example 1 and the solution was then applied by means of a doctor blade to a cotton fabric. The abrasion after 500 revolutions was 4.7 mg.

#### EXAMPLE 3

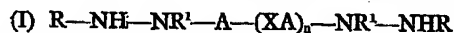
250 Grams of a polyester obtained from diethylene glycol and adipic acid (OH-number 43.2) were dehydrated for 1 hour *in vacuo* at 130°C. and heated in admixture with 6.9 g. of octadecane-1,2-diol with 40.6 g. of hexamethylene-1,6-diisocyanate for 1 hour at 110°C. The hot melt was dissolved in 150 g. of chlorobenzene, 3.20 g. of diethylene glycol in 4 g. of chlorobenzene were added and the reaction solution was kept for 25 minutes at 110°C. After cooling to 30°C., the solution was diluted with 500 g. of dimethyl formamide, NCO-number 0.65.

Another 380 g. of dimethyl formamide were added to 764 g. of this solution and, at 0. to 10°C. a solution of 4.28 g. of carbodi-hydrazide in 20 g. of water was added. The solution concentrated to a solid content of 36% had a viscosity of 170 poises at 20°C.

A coating prepared after addition of pigments and fillers, was extremely fast to light and showed good resistance to weather influences and a soft textile handle.

#### EXAMPLE 4

100 Grams of a polyester obtained from 50 mol% of ethylene glycol, 50 mol% of propylene-1,2-glycol and adipic acid (OH-number 53.2; Acid Number 2.0) were dehydrated for 1 hour at 130°C. *in vacuo* and thereafter heated with 20.1 g. of diphenyl methane-4,4'-diisocyanate for 60 minutes at 100°C. The hot melt was dissolved in 120 g. of chlorobenzene, a solution of 0.45 g. of butane-1,4-diol in 2 g. of absolute dioxane was added and the mixture was heated for another 60 minutes at 110°C. The NCO-content was then 0.805%. The solution was then diluted at 20°C. with 400 g. of dimethyl formamide and then the NCO-content was 0.282%.



in which A is a —CO—, —CS— or —SO<sub>2</sub>— group; R and R<sup>1</sup> are hydrogen atoms or alkyl or aryl radicals; X is an alkylene,

A solution of 2.64 g. of ω-amino-caproic acid hydrazide in 100 g. of dimethyl formamide at a temperature of 70°C. was then run-into 550 g. of the said solution while mixing well. A viscous solution was formed, which was concentrated to 25% solid content before incorporating coloured pigments and fillers by rolling.

Pigments and fillers were added to the solutions in the manner described in Example 1 and the solution was applied by means of a doctor blade to a cotton fabric. Soft, abrasion-resistant coatings are obtained.

#### EXAMPLE 5

100 Grams of the polyester described in Example 4 were dehydrated for one hour at 130°C. *in vacuo* and heated with 25.1 g. of diphenyl methane-4,4'-diisocyanate for 60 minutes at 100°C. The hot melt was dissolved in 120 g. of chlorobenzene, a solution of 0.45 g. of butane-1,4-diol in 2 g. of absolute dioxane was added and the combined solution was heated for another 60 minutes at 100°C. The NCO-content of the solution was 1.30%.

A solution of 4.38g. of ω-hydroxy butyric acid hydrazide in 100 g. of absolute dioxane at a temperature of 85° was added to 240 g. of this solution at 20°C. while stirring well. The solution became cloudy and distinctly more viscous. The reaction mixture was now heated for 20 minutes at 100°C. The viscous, opaque mass (36.5% solid content) had pigments and fillers added thereto in the manner described in Example 1 and was applied by means of a doctor blade to a cotton fabric, and freed from the solvents in a heating chamber at 110°C.

#### WHAT WE CLAIM IS:—

1. A process for the production of polymers comprising urethane and semi-carbazide groupings and which can be shaped from solution, which comprises reacting, in a melt or in solution, a substantially linear isocyanate-modified polyhydroxyl compound having a molecular weight of 500 to 5000 and containing terminal NCO-groups with 10 to 90% (calculated on the NCO-content of the isocyanate modified polyhydroxyl compound) of a polyhydric alcohol and thereafter reacting the prepolymer formed with 90 to 110% (calculated on the remaining NCO-content) of one or more compounds of the general formula

arylene or aralkylene radical which may be interrupted by hetero atoms or X is an —OYO— or —NH—Y—NH— radical in

- (I) or a  $\text{—YO—}$  or  $\text{—Y—NH—}$  radical in (II) or (III); Y is a divalent organic radical; and  $n$  is 0 or 1.
- 5 2. A process as claimed in claim 1, wherein the isocyanate-modified polyhydroxyl compound containing terminal NCO-groups is one which has been obtained from a polyhydroxy compound with such a quantity of polyisocyanate that 125 to 250 parts by weight of NCO-groups in the polyisocyanate were present to 34 parts by weight of hydroxy groups in the polyhydroxy compound.
- 10 3. A process as claimed in claim 1 or claim 2, wherein the reaction of the isocyanate-modified polyhydroxyl compound with the polyhydric alcohol is carried out at temperatures between 70 and 110°C.
- 15 4. A process as claimed in any of the preceding claims, wherein pigments and/or fillers are added to the polymer produced.
5. A process for the production of polymers, substantially as described with reference to any of Examples 1 to 3.
6. A process for the production of polymers, substantially as described with reference to Examples 4 or 5. 25
7. Polymers when produced by the process claimed in any of the preceding claims.
8. A process for coating a support, especially a textile, which comprises applying a layer of the polymer claimed in claim 7 to a support. 30
9. Supports, especially textiles, when coated with the polymer claimed in claim 7.

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